Letters to the Editor

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Infrared spectrum of dichlorosilicon-phthalocyanine

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Phthalocyanines belong to an important class of organic photo- and semi-conductors Besides they are involved in a very important group of biological molecules, chlorophyll and hemoglobin in particular There is extensive literature on the infrared spectra, between 4,000 cm^{-1} and 400 cm^{-1} of α- and β-polymorphic forms of various phthalocyanines (Gurnovich *et al* 1963 Sidarov & Kotlyar 1961)

Bloor *et al* (1964) have pointed out the major differences between the spectra of metal free and metal phthalocyanines. However, the spectra of metal phthalocyanines are in general very similar to those of the parent. In dichlorosilicon phthalocyanine ($SiCl_2Pc$) the central metal atom has two chlorine atoms linked to it Thus it differs from other metal phthalocyanines, and the situation is quite similar to uranyl phthalocyanine [UO_2Pc]. The purpose of this note is to report the infrared and far infrared spectra of $SiCl_2Pc$ and to confirm that in the molecule the two chlorine atoms in fact remain attached to the silicon atom The material under investigation was prepared by heating phthalonitrile, tetrachlorosilane and and quinoline in a sealed Carius tube for several hours. The crystalline compound was isolated from the tars by washing with dimethyl formamide and acetone The method yielded good single crystals of dichlorosilicon-phthalocyanine Nitrogen analysis : theoretical 18.33 analysed 18.37.

The spectra of the $SiCl_2Pc$ prepared as KBr pellets, were recorded from 4,000 cm^{-1} to 300 cm^{-1} on a Perkin Elmer model 521 infrared spectrophotometer, and from 300 cm^{-1} to 100 cm^{-1} on a Perkin Elmer model 301 F.I.R. Spectrophotometer. Using the numbering system of Sidorov and Kotlyar (1961) we have

listed various bands of $SiCl_2Pc$ We have also included in these tables the spectra of UO_2Pc as reported by Bloor *et al* (1964) The I.R spectrum of dichlorosilicon-pthhalocyanine is very similar to UO_2–and metal-phthalocyanines (Bloor *et al* 1964) except that some of the bands are silightly shifted in position The notable difference from metal-phthalocyanines are the strong bands in dichlorosilicon phthalocyanine in the 600 cm ^{1} and 350 cm^{-1} region. The situation seems to arise from a shift in the symmetry of the molecule It is well known (Gurnovich *et al* 1963)

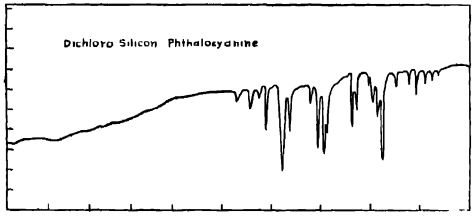

Figure 1 I R Spectrum of dichloro-silicon phthalocyanine

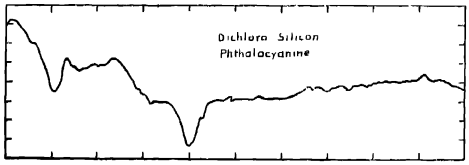

Figure 2. F.I R Spectrum of dichloro-silicon phthalocyanine

that in the case of porphyrins one should expect five bands corresponding to N.H vibrations if the symmetry of the molecule is C_{2v} but only three if the symmetry is D_{2h}. Therefore, the increase in the number of absorption bands in the case of dichlorosilicon and uranyl phthalocyanines may be due to departure from D_{4h} molecular symmetry of metal phthalocyanines. This departure is expected towards lower symmetry. This seems reasonable if one remembers that the spectrum of $SiCl_2Pc$ and UO_2Pc are essentially similar to each other and both have two extra atoms besides the central metal atom. However, with the limited evidence it is not possible to assign any speific symmetry to the molecule.

Metal-ligand stretching and bending frequencies are usually few in number, and have been assigned below 300 cm^{-1}. Our spectra in the 300 cm^{-1}-100 cm^{-1} region is the second reported for any of the phthalocyanine. It shows only two clear bands at 122 cm^{-1} and 180 cm^{-1}. The bands at 130 cm^{-1}, 142 cm^{-1}, 240 cm^{-1} and 248 cm^{-1} are only speculative and cannot be established firmly. Looking at the spectra reported by Bloor *et al* (1964) along with those reported here one may guess that 122 cm^{-1} band is a Si-N band and the one at 180 cm^{-1} is due to Cl-Si-Cl bending frequency

TABLE 1 Infrared spectra bands in cm^{-1}

Band No	UO_2Pc Bloor *et al*	$SiCl_2Pc$	Band No.	UO_2Pc Bloor *et al*	$SiCl_2Pc$
32	1605	1605	17a		
31a	1575		17b	1030	1060
31b	1520	1528	16	1020	
31c			15	950	
30a	1510		14	930	912
30b	1490		13	900	880
29			12	868	
28		1471	12		805
27a		1428	9	775	781
27b	1410		8	765	759
37c	1350		7	727	
26	1331	1332	6a	720	731
25			6b	712	
24	1300wk		5	704	
23a	1285	1288	4a	675	
23b			4b	640	644
22a			4c	620	
22b			3		575
21	1150	1162	2a		532
20a			2b	460	464
20b	1120	1120	1a	415	427
19					381
18	1072	1080			

TABLE 2. Far infrared spectra bands in cm^{-1}

UO_2Pc Bloorr *et al*	$SiCl_2Pc$	UO_2Pc Bloor *et al*	$SiCl_2Pc$
306	304	244	230*
—	283*	-	180 (Cl-Si-Cl Band)
278s		164ms	—
—		147ms	122
258	250*		

Abbreviations . s-strong, ms-moderately strong.

*These peaks are very weak and cannot be confirmed beyond doubt.

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Crystal and molecular structure of p-dimethylamino-benzaldehyde hydrobromide

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p-Dimethylaminobenzaldehyde ($C_9H_{11}NO$) is a biologically important compound. Among its various biological functions mention may be made of its special role in differentiating between true scarlet fever and serum eruptions. The structural analysis of this compound in the form of its different hydrohalides and metal complexes has been undertaken by us with an ultimate view to correlate the structural features with biological functions. This short communication deals with the crystal structure of *p*-dimethylaminobenzaldehyde hydrobromide.

The compound was prepared in our laboratory by treating *p*-dimethylaminobenzaldehyde with 30%HBr. Single crystals were grown by slow evaporation of an aqueous solution of this compound between 35°-40°C. The crystals thus grown are needle shaped, *c*-axis being parallel to needle axis. As the crystal was found to be unstable under normal atmospheric condition, it was placed in a sealed thin walled glass capillary while taking X-ray photographs. The crystals belong to monoclinic space group $P2_{1/c}$ having unit cell dimensions

$$a = 12.65\text{Å}$$
$$b = 10.20\text{Å}$$
$$c = 7.42\text{Å}$$
$$\beta = 90°30'$$

Density data ($\rho_m = 1.54$ gm/cc, $\rho_c = 1.59$ gm/cc) indicate that there are four formula units of $(C_9H_{11}NO)HBr$ per unit cell. Multiple-film equi-inclination Weissenberg technique was used to collect three-dimensional intensity data for layers